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Communication

Iron-Catalyzed Alkyne Carboamination via an Isolable Iron Imide Complex

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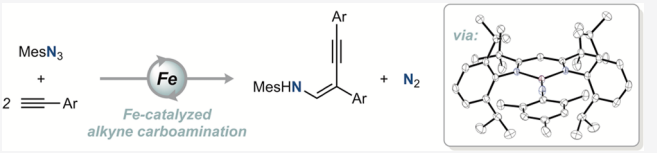
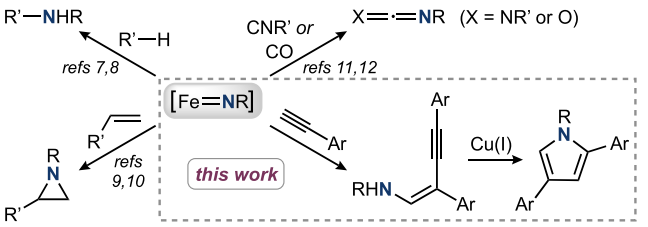
ABSTRACT: Transition metal imide-mediated C−N bond formation is a powerful strategy for the introduction of nitrogen into organic compounds. We have discovered that the reaction of *N*-mesityl(*β*-diketiminato)iron imide complex ^{tBu}LFeNMes (^{tBu}L = 3,5-bis(2,6-diisopropylphenylimino)-2,2,6,6-tetramethylheptyl and Mes = 2,4,6-trimethylphenyl) with a terminal alkyne substrate gives a *β*-alkynyl enamine product by a novel alkyne carboamination process. Stoichiometric experiments revealed a catalyst deactivation pathway involving generation of the acetylide complex, ^{tBu}LFeCCPh, and mesityl amine ($MesNH_2$) from the acetylene complex, ^{tBu}LFe(HCCPh), and mesityl azide ($MesN_3$). This reactivity is suppressed in the presence of coordinating additive 4-*tert*-butylpyridine (^{t}BuPy), likely through formation of the four-coordinate complex ^{tBu}LFe(HCCPh)(^{t}BuPy). These insights were instrumental in identifying reaction conditions that allow for turnover of the iron catalyst.



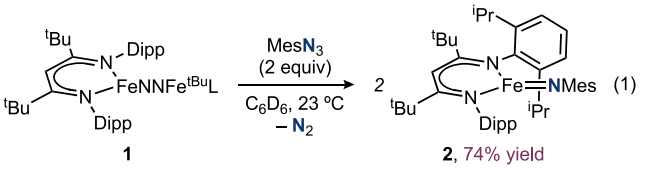
The incorporation of nitrogen into organic molecules is an undeniably important goal in chemical synthesis given the ubiquity of nitrogen in biologically active compounds.[1] One valuable approach involves the construction of C−N bonds via the transfer of nitrene groups (NR) from transition metal imide complexes.[2] Methods that take advantage of imide complexes based on iron[3] are especially attractive given that iron is nontoxic[4] and the most abundant transition metal in Earth's crust.[5] Iron imides (Fe = NR, Scheme 1) are proposed as the active species in a variety of catalytic group transfer reactions,[6] including C−H amination,[7,8] alkene aziridination,[9,10] and carbodiimide and isocyanate formation (Scheme 1).[11,12] Stoichiometric studies like those described by the Betley[8d,13] and Holland[11,12] groups support the intermediacy of iron imide species in these catalytic transformations.

Scheme 1. Iron Imides in C−N Bond-Forming Reactions



Herein, we report a novel alkyne carboamination process in the reaction of an iron imide complex with a terminal alkyne substrate (Scheme 1).[14,15] Stoichiometric studies provided essential insights that allowed us to render this process catalytic with respect to iron. The reaction generates new C−N and C−C bonds in the *β*-alkynyl enamine product, a compound that we found can also be cyclized in the presence of a copper(I) salt[16] to form the 2,4-disubstituted pyrrole (Scheme 1; see the Supporting Information),[17,18] a common substructure in medicinal chemistry.[19] In addition to incorporating a new class of substrate, the chemistry described here couples the nitrene group of an iron imide to two substrate equivalents, setting it apart from previously reported iron imide chemistry (Scheme 1).

Our group is interested in iron imide complexes for their potential as catalytic species in iron-catalyzed C−N bond formation. Several examples of isolable, mononuclear iron imides[20] have been described since Peters' seminal report.[20f] Exceptional work from the Holland group on iron imides supported by *β*-diketiminate ligands[11,21−23] suggested the possibility of accessing a related complex, ^{tBu}LFeNMes (**2**, eq 1). Indeed, reaction of dinitrogen precursor ^{tBu}LFeNNFe^{tBu}L



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(**1**, eq 1)[24] and mesityl azide ($MesN_3$) leads to formation of **2** in 74% yield. Complex **2** is relatively stable, with $t_{1/2} \sim 4$ days in C_6D_6 solution at 23 °C. Magnetic susceptibility measurements support an $S = 3/2$ ground state, consistent with an intermediate-spin iron(III) species and in agreement with data previously reported for other (β-diketiminato)iron imides.[11,21−23]

The stability of complex **2** allowed us to determine its molecular structure by X-ray crystallography (Figure 1).

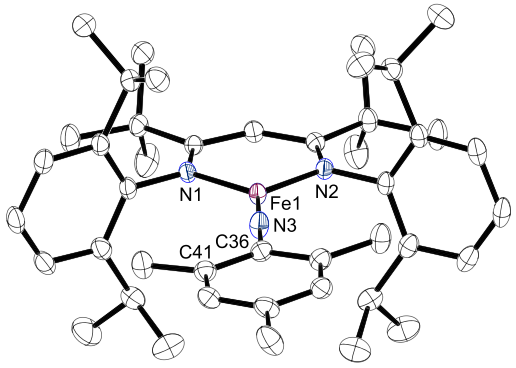
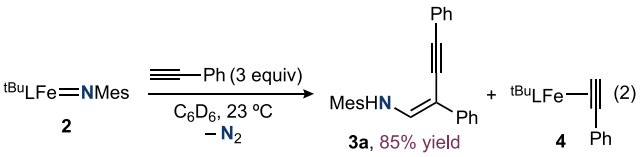


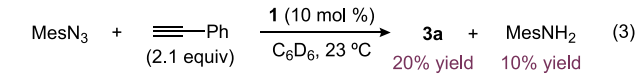
Figure 1. Molecular structure of ^{tBu}LFeNMes (**2**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distance (Å) and angles (deg) for **2**: Fe1−N3, 1.7097(1); Fe1−N3−C36, 178.52(9); N1−Fe1−N2, 96.67(4); N1−Fe1−N3, 131.37(4), N2−Fe1−N3, 131.97(4).

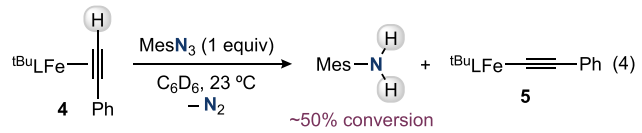
Similar to the structures of related *N*-adamantyl (β-diketiminato)iron imides,[22,23] **2** contains a three-coordinate iron center that is planar, with bond angles that sum to 360.0(2)°. The Fe═N bond is longer (1.7097(1) Å) and the Fe═N−C bond angle is remarkably linear (178.52(9)°) compared to these examples[22,23] (1.670(2) Å and 170.4 (2)°, 1.700 (5) Å and 151.2 (5)°, respectively). Interestingly, the *N*-aryl substituent is nearly coplanar with the ligand plane, with a dihedral angle of 4.5(2)° between N1−Fe1 and C36−C41 bonds, an observation that may result from steric[25] and/or electronic factors.

The unusual structural properties of **2** hinted at the possibility for new reactivity. We were particularly interested in the reaction of **2** and phenylacetylene, a substrate that contains both an activated C−H bond and a π-system. To this end, **2** was exposed to 1 equiv of phenylacetylene in C_6D_6 solution. Analysis of the reaction mixture showed total consumption of phenylacetylene after 15 min as well as formation of a new organic product, identified as β-alkynyl enamine **3a** as a single *Z*-isomer (eq 2). The structure of **3a** as the enamine tautomer was confirmed by thorough spectroscopic analysis, including ^{1}H−^{15}N HSQC NMR (see the Supporting Information).

Complete conversion of the imide complex occurs within 15 min when 3 equiv of phenylacetylene are added to **2** (eq 2). In this case, **3a** forms cleanly (85% yield by ^{1}H NMR) alongside a single organometallic product, identified as the phenylacetylene complex, ^{tBu}LFe(HCCPh) (**4**, eq 2),[25] by ^{1}H NMR. This result is encouraging in the context of a potential catalytic reaction: the iron center in **4** is in the same formal +1 oxidation state[26] as the dinitrogen precursor **1** used to generate imide complex **2** (eq 1). However, an attempted catalytic reaction performed by addition of $MesN_3$ followed by 2.1 equiv of phenylacetylene to 10 mol % of **1** (20 mol % of Fe)



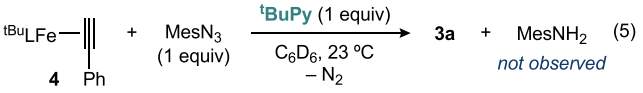




leads to **3a** in a single turnover (20% yield by ^{1}H NMR, eq 3).[27]

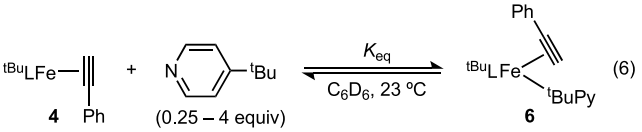
The lack of catalytic reactivity shown in eq 3 prompted investigation of the proposed turnover step, conversion of ^{tBu}LFe(HCCPh) (**4**) to ^{tBu}LFeNMes (**2**). Rather than transfer of the NMes group to iron to generate **2**, reaction of **4** and 1 equiv of $MesN_3$ leads to formation of 2,4,6-trimethylaniline, $MesNH_2$, in approximately 50% conversion with respect to $MesN_3$. The major organometallic product was identified as the iron acetylide complex, ^{tBu}LFeCCPh (**5**, eq 4),[28] by ^{1}H NMR. This result is fully consistent with deactivation of the iron catalyst and the formation of $MesNH_2$ shown in eq 3.

The reactivity in eq 4 presents a serious problem for rendering alkyne carboamination catalytic with respect to iron. Considering how to solve this problem, we hypothesized that a coordinating additive could suppress this catalyst-deactivating process through coordination to **4**.[29] To evaluate this idea, 1 equiv of ^{t}BuPy was added to the reaction of **4** and $MesN_3$ (eq 5). Carboamination reactivity is recovered and the process in



eq 4 is avoided under these conditions, evidenced by the presence of **3a** and the absence of $MesNH_2$ in the reaction mixture (eq 5).

We propose the coordinating additive takes effect through the formation of a four-coordinate complex, ^{tBu}LFe(HCCPh)-(^{t}BuPy) (**6**, eq 6). Isolation of the product of the reaction of **4**



and 1 equiv of ^{t}BuPy from a concentrated pentane solution at −35 °C and analysis by X-ray crystallography confirmed the molecular structure of complex **6** in the solid state (Figure 2; see the Supporting Information for further details). NMR experiments also point to the existence of **6** in solution. The ^{1}H NMR spectra of reactions of **4** ($[\mathbf{4}]_0$ = 20 mM) in the presence of varied concentrations of ^{t}BuPy show sets of paramagnetic peaks similar to those observed for **4** alone, plus three additional peaks that can be assigned to the ^{t}BuPy ligand. The chemical shifts of these peaks show a concentration dependence on ^{t}BuPy, consistent with an equilibrium between

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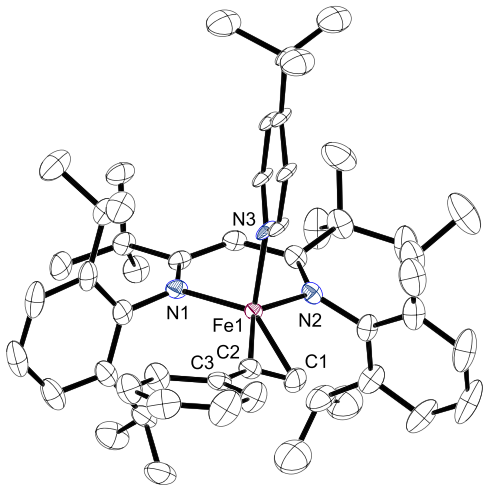


Figure 2. Molecular structure of ^{tBu}LFe(HCCPh)(^{t}BuPy) (**6**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **6**: Fe1−C1, 1.956(4); Fe1−C2, 1.992(4); Fe1−N3, 2.097(7); C1−C2, 1.264(7); C1−C2−C3, 146.0(4), N1−Fe1−N3, 99.1(2); N2−Fe1−N3, 96.9(2).

three-coordinate **4** and four-coordinate **6** (Figure 3). Plotting the change in chemical shift versus $[^{t}\text{BuPy}]_0$ revealed an equilibrium constant (K_{eq}) of 12.4 ± 0.3 M^{-1} for the reaction shown in eq 6 (see the Supporting Information).[30]

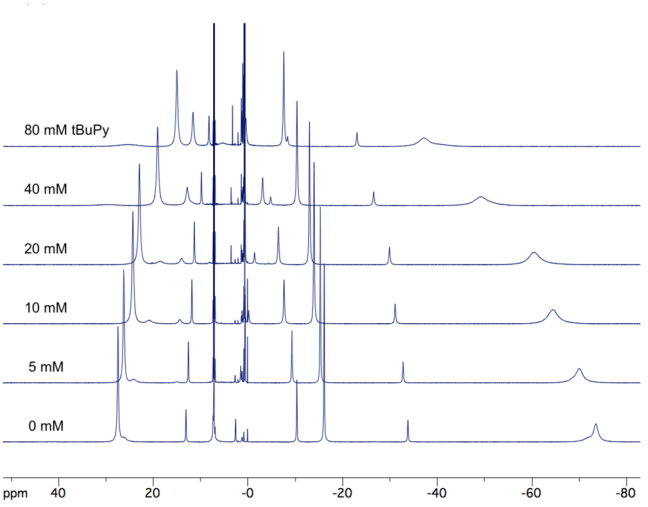
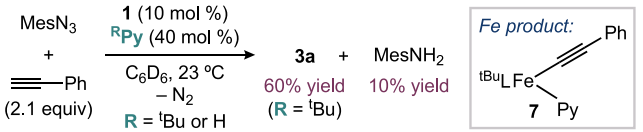


Figure 3. ^{1}H NMR spectra of the reactions shown in eq 6 at the indicated initial concentrations of ^{t}BuPy and 20 mM **4**.

Certainly, a coordinating additive has the potential to interact with other iron species present in the catalytic reaction mixture. We were especially interested in the possible coordination of ^{t}BuPy to **2**, given the higher decomposition rate of ^{Me}LFeNAd(^{t}BuPy) (^{Me}L = 2,4-bis(2,6-diisopropylphenylimino)pentyl and Ad = 1-adamantyl) versus ^{Me}LFeNAd ($t_{1/2}$ ∼ 30 min versus 2 days, respectively).[22] ^{1}H NMR analysis of the reaction of 1 equiv of ^{t}BuPy and **2** supports the formation of a four-coordinate complex, ^{tBu}LFeNMes(^{t}BuPy) (see the Supporting Information). This compound is less stable than three-coordinate complex **2** ($t_{1/2}$ ∼ 1.5 h versus 4 days, respectively). Fortunately, carboamination is faster than decomposition in the presence of the phenylacetylene substrate. That is, simultaneous addition of 1 equiv of ^{t}BuPy and 3 equiv of phenylacetylene to **2** leads to formation of **3a**, as observed by ^{1}H NMR (see the Supporting Information).

Importantly, the result in eq 5 implies that **4** can be converted to **2** in the presence of a ^{t}BuPy additive, thus closing the catalytic cycle. When a catalytic reaction is performed by adding a solution of $MesN_3$, 2.1 equiv of phenylacetylene, and 40 mol % of ^{t}BuPy to 10 mol % of **1**, product **3a** forms in 60% yield by ^{1}H NMR (Scheme 2). The remainder of the reaction

Scheme 2. Catalytic Carboamination in the Presence of Coordinating Additives



mixture sheds light on the reason for this moderate yield. In addition to **3a**, $MesNH_2$ is generated in 10% yield, indicating that catalyst deactivation still competes with carboamination in the presence of ^{t}BuPy. Furthermore, the iron-containing product isolated at the end of the reaction with pyridine (Py) as the additive[31] was identified as ^{tBu}LFeCCPh(Py) (**7**, 67% isolated yield based on Fe, Scheme 2) by X-ray crystallography (Figure 4). Complex **7** presumably arises from coordination of Py to **5**, which is generated by the process in eq 4.

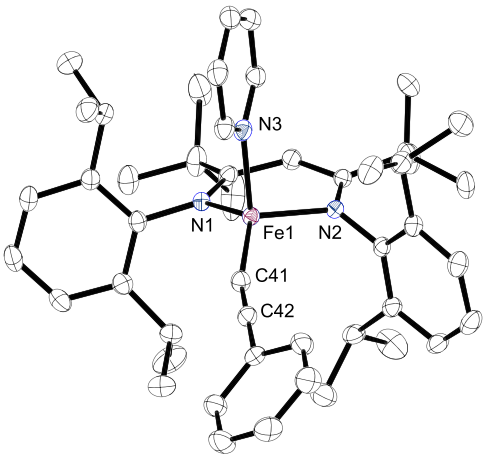


Figure 4. Molecular structure of ^{tBu}LFe(CCPh)(Py) (**7**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **7**: Fe1−C41, 2.0126(1); Fe1−N3, 2.1229(1); C41−C42, 1.212(2); Fe1−C41−C42, 165.58(1), N3−Fe1−C41, 104.86(5); N1−Fe1−N3, 102.87(4); N2−Fe1−N3, 102.39(4).

A proposed catalytic cycle illustrating potential intermediate complexes that have been observed in stoichiometric experiments is shown in Scheme 3. Iron imide complex **2** reacts with 3 equiv of phenylacetylene by carboamination to give β-alkynyl enamine **3a** and phenylacetylene complex **4**. From **4**, two pathways are possible. Catalyst deactivation through interaction with $MesN_3$ can occur to form $MesNH_2$ and acetylide complex **5**, which can coordinate the pyridine additive to give **7**. Alternatively, **4** may engage the pyridine additive to generate

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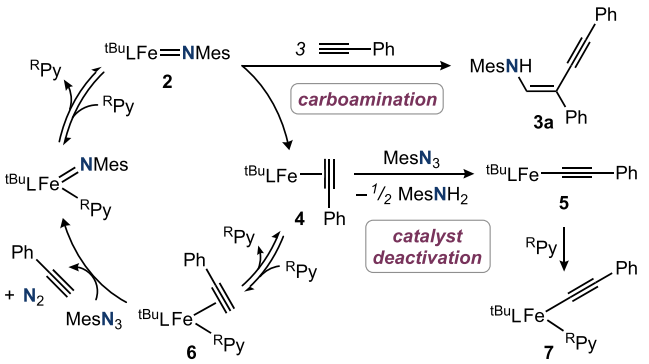
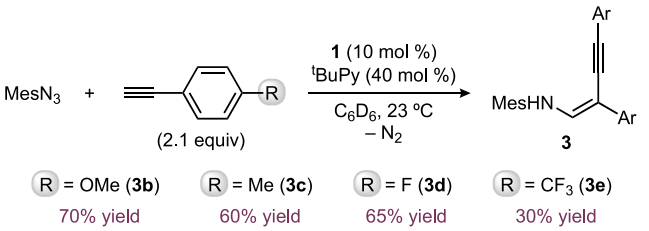
Scheme 3. Proposed Catalytic Cycle Involving Potential Intermediates Observed in Stoichiometric Experiments



four-coordinate complex **6**. Release of phenylacetylene and reaction with $MesN_3$ leads to pyridine-bound imide complex ^{tBu}LFeNMes(^{R}Py), which is in equilibrium with imide complex **2**. The detailed mechanisms of carboamination and catalyst deactivation are both subjects of current work in our lab.

A preliminary reaction scope evaluating the carboamination reactivity of various 4-substituted arylacetylene derivatives is shown in Scheme 4. Electron-rich substrates 4-methoxy- and 4-

Scheme 4. Preliminary Scope of the Arylacetylene Substrate (Yields Determined by ^{1}H NMR)



methylphenylacetylene couple to $MesN_3$ to give β-alkynyl enamines **3b** and **3c** in moderate yields (70 and 60%, respectively, by ^{1}H NMR). 4-Fluorophenylacetylene is also a competent substrate for alkyne carboamination, delivering **3d** in 65% yield. The reaction of $MesN_3$ and 4-(trifluoromethyl)-phenylacetylene, on the other hand, leads to **3e** in only 30% yield, suggesting that the electron-withdrawing substituent is detrimental to reactivity. Products **3b**−**3e** can be converted to the 2,4-disubstituted pyrroles by copper(I)-catalyzed cyclization (see the Supporting Information).

We have discovered that the *N*-mesityl(β-diketiminato)iron imide complex ^{tBu}LFeNMes interacts with phenylacetylene by alkyne carboamination to give a β-alkynyl enamine product. Efforts to render the reaction catalytic in iron identified a competing process that is responsible for catalyst deactivation. Stoichiometric studies revealed that this reactivity can be avoided in the presence of a pyridine additive, presumably through coordination and formation of a four-coordinate complex. Further studies are underway to fully elucidate the mechanisms of carboamination and catalyst deactivation and to explore the scope of this exciting chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00454.

Complete experimental procedures, characterization data, and spectra (PDF)

Accession Codes

CCDC 2074416−2074417 and 2096003 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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